

## Preparation and Characterization of Carbon Nitride Nanocage

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A novel highly ordered three dimensional cage type mesoporous carbon nitride material (MCN-2 – CN nanocage) with very high surface area and pore volume has been prepared for the first time using three dimensional cage type mesoporous silica, SBA-16 as a template through a simple polymerization reaction between ethylenediamine and carbon tetrachloride. The material has been unambiguously characterized by various sophisticated techniques such as XRD, nitrogen adsorption, HRTEM, EELS, XPS, <sup>13</sup>C DD-MAS, and FT-IR spectroscopy. The XRD result reveals that MCN-2 possesses three dimensional structure with a *Im3m* space group. The specific surface area and pore volume of MCN-2 are significantly higher as compared to those of the template and MCN-1. Because of the excellent textural characteristic and cage type three dimensional porous structure, we believe that the MCN-2 could offer great potential for the applications, such as catalytic supports, gas storage, lubricants, biomolecule adsorption and drug delivery.

Key words: carbon nitride, SBA-16, mesoporous silica, nanocage

### 1. INTRODUCTION

Mesoporous materials with cage type three dimensional porous structure, namely, SBA-1, SBA-6 and SBA-16, have attracted a significant attention in the recent days owing to their excellent textural characteristics.<sup>1-3</sup> Among the cage type mesoporous materials, SBA-16, synthesized using a low cost polymeric F127 surfactant, has received much attention because of its three dimensional structure with a large cage type mesopores of diameter well above 5 nm, thicker pore walls, and excellent thermal and mechanical stabilities. This material has body centered cubic porous structure with eight nearest neighbor mesopores which are connected each other with their adjacent mesopores.<sup>1-4</sup> The above interesting structural features make it useful for many applications including catalysis, adsorption and separation. Several researchers have tried to make a cage type mesoporous carbon using SBA-16 as a hard template. However, most of them were failed to get a well-ordered mesoporous carbon because of narrow pore aperture between the adjacent cages of SBA-16. Recently, Kim et al. have successfully prepared a cage type mesoporous carbon material from SBA-16 by using a small size carbon precursor viz., furfuryl alcohol.<sup>5</sup> Carbon nitride (CN) is a well known and super hard material that has attracted worldwide attention because the incorporation of nitrogen atoms in the carbon nanostructure can enhance the mechanical, conducting, field emission, and energy storage properties.<sup>6-19</sup> By constructing CN materials with porous structure, many novel applications could emerge: from catalysis, to separation and adsorption of very bulky molecules, and to the fabrication of low dielectric devices. Very recently, Vinu et al. have successfully reported the preparation of uni-dimensional mesoporous CN (MCN-1) using SBA-15 as a template.<sup>20</sup> Unfortunately, this material

possesses very low surface area, pore volume and one-dimensional porous structure. Mesoporous CN (MCN) with three dimensional cage type pore systems promises access to an even-wider range of application possibilities because of their unique properties such as semi-conductivity, intercalation ability, hardness, etc.<sup>6-19</sup>. More importantly, the accessibility of the pores and the surface active sites are easily achievable in the three dimensional cage type porous structure. However, to the best of our knowledge, there are no reports on mesoporous carbon nitride having three dimensional cage type pore structure with a well-defined pore size and morphology (MCN-2). Here, we report for the first time the preparation of such a novel material through the polymerization reaction between ethylenediamine and carbon tetrachloride using SBA-16 as the template. It has been always a challenge to get well order mesoporous materials mainly carbon using SBA-16 as a template because of its porous structure. However, we optimized the synthetic procedure which was used in the synthesis of mesoporous carbon nitride using SBA-15 and could get a well ordered three dimensional mesoporous cage type carbon nitride. Interestingly, we found that the surface area, pore volume and pore size of MCN-2 are much higher as compared to that of MCN-1.

### 2. EXPERIMENTAL SECTION

*Synthesis of three dimensional cage type mesoporous silica template, SBA-16:* Triblock copolymers Pluronic F127 (EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>,  $M_{av}$  = 12600) was used as received from Sigma. Sodium metasilicate nonahydrate (Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O) and hydrochloric acid (c-HCl, 37.6%) were obtained from Fisher Scientific. In a typical synthesis, 16 g of a 10% aqueous solution of F127 was poured into 26.6 g of distilled water and then 4.71 g of sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O) was added at 40 °C

with magnetic stirring to yield a clear solution. To this solution, 13 g of concentrated hydrochloric acid (37.6%) was quickly added with vigorous stirring to obtain a gel. The molar composition of the gel mixture was  $1.0 \text{ SiO}_2 : 3.17 \times 10^{-4} \text{ F127} : 6.68 \text{ HCl} : 137.9 \text{ H}_2\text{O}$ . The gel solution was stirred for 24 hours at  $37^\circ\text{C}$  before loaded into an autoclave, and heated for 24 hours at  $100^\circ\text{C}$ . The solid product was filtered, dried at  $120^\circ\text{C}$  overnight, and calcined in air at  $500^\circ\text{C}$ .

**Synthesis of three dimensional mesoporous carbon nitride, CN nanocage (MCN-2):** 0.5 g of calcined SBA-16<sup>21</sup> was added to a mixture of ethylenediamine (1.35 g) and carbon tetrachloride (2.31 g). The resultant mixture was refluxed and stirred at  $90^\circ\text{C}$  for 6 hours. Then, the obtained dark brown colored solid mixture was placed in a drying oven for 12 hours, and ground into fine powder. The template-carbon nitride polymer composites were then heat treated in a nitrogen flow of 50 ml per minute at  $600^\circ\text{C}$  with the heating rate of  $3.0^\circ\text{C min}^{-1}$  and kept under these conditions for 5 h to carbonize the polymer. The mesoporous carbon nitride (MCN-2) was recovered after dissolution of the SBA-16 silica framework in 5 wt % hydrofluoric acid, by filtration, washed several times with ethanol and dried at  $100^\circ\text{C}$ . It is important to note that when the synthesis procedure for the MCN-1 was used<sup>20</sup>, no solid product was obtained.

### 3. CHARACTERIZATION

The powder X-ray diffraction patterns of SBA-16 and MCN-2 materials were collected on a Rigaku diffractometer using  $\text{CuK}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation. The diffractograms were recorded in the  $2\theta$  range of  $0.8$  to  $10^\circ$  with a  $2\theta$  step size of  $0.01^\circ$  and a step time of 1 second. Nitrogen adsorption and desorption isotherms were measured at  $-196^\circ\text{C}$  on a Quantachrome Autosorb 1 sorption analyzer. All samples were outgassed for 3 hours at  $250^\circ\text{C}$  under vacuum ( $p < 10^{-5} \text{ hPa}$ ) in the degas port of the adsorption analyzer. The specific surface area was calculated using the BET model. The pore size distributions were obtained from the desorption branch of the nitrogen isotherms. The diameter of the cages in SBA-16 and MCN-2 was calculated using equation (1) which was recently proposed by Ravikovitch and Niemark<sup>22</sup>

$$D_{\text{me}} = a \cdot (6\epsilon_{\text{me}}/\pi v)^{1/3} \quad (1)$$

In equation (1),  $D_{\text{me}}$  is the diameter of the cavity of a cubic unit cell of length  $a$ ,  $\epsilon_{\text{me}}$  is the volume fraction of a regular cavity and  $v$  is the number of cavities present in the unit cell (for  $Im3m$  space group,  $v = 2$ ).

The wall thickness of the cage type mesoporous materials was calculated using equation (2) which was derived from equation (1)

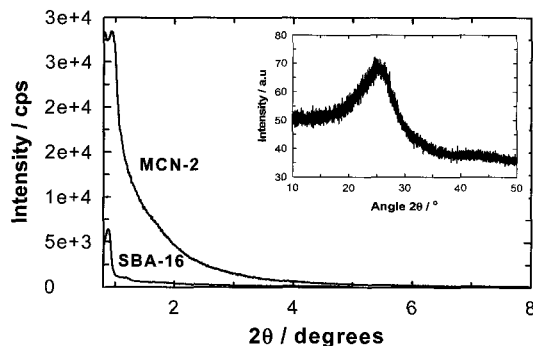
$$h = 2 a_0^3/\pi D_{\text{me}}^2 v - D_{\text{me}}/3 \quad (2)$$

The HRTEM images were obtained using JEOL-3000F and JEOL-3100FEF field emission high-resolution transmission electron microscopes equipped with a Gatan-766 electron energy-loss spectrometer (EELS). The preparation of samples for HRTEM analysis involved sonication in ethanol for 2 to 5 min and

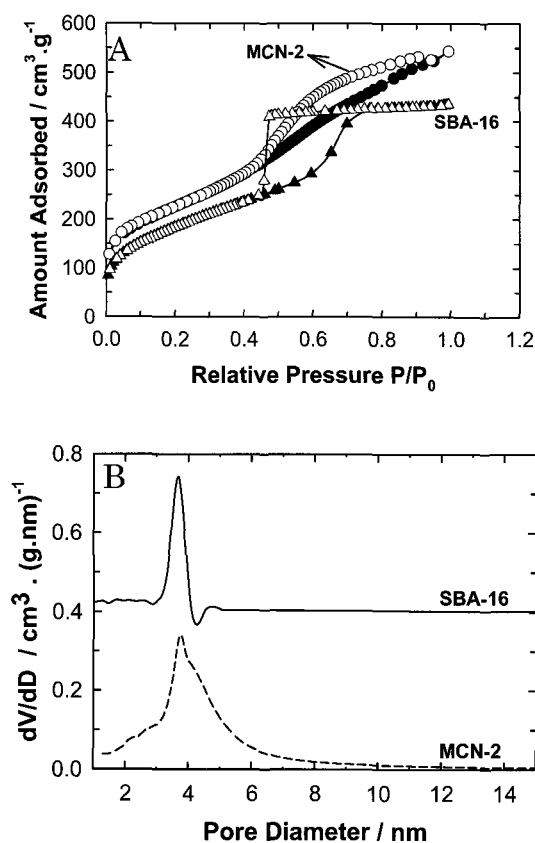
deposition on a copper grid. The accelerating voltage of the electron beam was 200 kV. Elementary analysis was done using an Analyst AA 300 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI 5400 instrument with a 200 W  $\text{MgK}\alpha$  probe beam to characterize the samples. The spectrometer was configured to operate at high resolution with pass energy of 20 eV. Prior to the analysis, the samples were evacuated at high vacuum and then introduced into the analysis chamber. Survey and multi-region spectra were recorded at  $\text{C}_{1s}$  and  $\text{N}_{1s}$  photoelectron peaks. Each spectra region of photoelectron interest was scanned several times to obtain good signal-to-noise ratios. FT-IR spectrum of MCN-2 was recorded on a Nicolet Nexus 670 instrument by averaging 200 scans with a resolution of  $2 \text{ cm}^{-1}$  measuring in transmission mode using the KBr self-supported pellet technique. The spectrometer chamber was continuously purged with dry air to remove water vapor.

### 4. RESULTS AND DISCUSSION

Figure 1 shows the powder XRD pattern of MCN-2 along with the parent mesoporous silica, SBA-16. It can be seen that SBA-16 mesoporous silica template exhibits well resolved (110), (200) and (211) reflections, characteristics of the body centered three dimensional cubic space group  $Im3m$ . The powder XRD pattern of MCN-2 also shows a sharp low angle peak and a broad higher order peak and is almost similar to that obtained for the SBA-16 mesoporous silica template (Figure 1). The results confirm that three dimensional mesoporous cage structure of the silica template is successfully replicated to the MCN-2 sample. It is interesting to note that the intensity of the (110) peak of MCN-2 is much higher than that of the silica template. The unit cell parameter of the MCN-2 is calculated using the formula  $2^{1/2}d_{110}$  to be 13.4 nm. The higher angle powder diffraction pattern of MCN-2 is also shown in Figure 1B. The samples exhibits a single broad diffraction peak (inset) near  $25.47^\circ$  ( $d = 3.42 \text{ \AA}$ ). This peak is almost similar to the characteristic 002 basal plan diffraction peak in the nonporous carbon nitride spheres. This reveals the presence of turbostratic ordering of the carbon and nitrogen atoms in the graphene layers of MCN-2.



**Figure 1:** Powder XRD patterns of SBA-16 and MCN-2 (inset: higher angle powder XRD pattern of MCN-2).



**Figure 2:** Nitrogen adsorption-desorption isotherms (A) and BJH desorption pore size distributions (B) of SBA-16 and MCN-2 (closed symbols: adsorption; open symbols: desorption).

The nitrogen adsorption isotherm of MCN-2 in comparison to that of the parent silica template is shown in Figure 2A. Both the materials exhibit type IV isotherm with a broad H2 hysteresis loop at the high relative pressure region which is typical for the well ordered large cage type mesoporous material. The amount of nitrogen adsorbed on the MCN-2 sample is much higher than that of the parent mesoporous silica template. As can be seen from Figure 2A, MCN-2 features a broader capillary condensation step than that of its parent silica, indicating a slight disorder in the porous matrix in the MCN-2. From the Table 1, it can also be seen that the specific surface area and the specific pore volume of MCN-2 are much higher than those of the template and the one dimensional mesoporous carbon nitride, MCN-1, prepared from the one dimensional mesoporous silica template, SBA-15.<sup>20</sup> The wall thickness and cage diameter of MCN-2 are lower than those of its parent silica template. This could be mainly due to the incomplete filling of carbon and nitrogen sources in the cages of SBA-16 silica template. It is also important to note that no well ordered cage type mesoporous carbon nitride was obtained when our previous synthesis procedure for MCN-1 was used in this study. This could mainly be attributed to difference in the pore structure and the diameter of SBA-16 as compared to SBA-15 template. To the best of our knowledge, this is the first report on the preparation of three dimensional cage type mesoporous carbon nitride materials with a very high specific surface area and specific pore volume

which are crucial for the applications in adsorption and fuel cells.

**Table 1:** Textural parameters of MCN-2, SBA-16, MCN-1 and SBA-15

Material	$a_0$ / nm	SA / m <sup>2</sup> /g)	PV / cm <sup>3</sup> ·g - <sup>1</sup> )	C D / nm <sup>22</sup>	W T/ nm <sup>22</sup>
MCN-2	13.4	810	0.81	10.8	2.91
SBA-16	14.2	750	0.65	11.3	3.30
MCN-1 <sup>20</sup>	9.5	505	0.55	-	4.52
SBA-15 <sup>20</sup>	10.3	910	1.20	-	1.30

SA – Surface Area; PV – Pore Volume; CD – Cage Diameter; WT – Wall Thickness

The BJH desorption pore distribution of MCN-2 along with its parent mesoporous silica is shown in Figure 2B. Although the pore diameter of the MCN-2 is almost similar to that of SBA-16, the pore size distribution of MCN-2 is a little bit broader than that of the SBA-16. This could be mainly attributed to a slight mesostructural disorder in the MCN-2 materials mainly due to the incomplete filling of the CN polymer matrix inside the pores of the silica template. HRTEM image of MCN-2 taken along the [110] in which the bright contrast strips on the image represent the pore wall images, whereas dark contrast cores display empty channels exhibits well ordered mesoporous structure with a regular intervals of linear array of mesopores throughout the samples which is characteristics of well ordered SBA-16 mesoporous silica (not shown). The nature, chemical composition, and the purity of the MCN-2 were obtained by XPS and FT-IR spectroscopic measurements. It has been found from XPS and IR results that most of the carbon atoms in the MCN-2 materials are  $sp^2$  bonded with nitrogen as in the aromatic ring attached to the terminal  $NH_2$  groups (not shown). CHN and EELS analysis showed that the ratio of carbon and nitrogen in the materials is around 4.1.

## 5. CONCLUSION

In summary, a highly ordered three dimensional cage type mesoporous carbon nitride material, CN nanocage with very high surface area and pore volume has been prepared for the first time using three dimensional cage type mesoporous silica, SBA-16 as a template through a simple polymerization reaction between ethylenediamine and carbon tetrachloride. The specific surface area and pore volume of CN nanocage are significantly higher as compared to those of the template and MCN-1. Because of the excellent textural characteristic and cage type three dimensional porous structure, we believe that the MCN-2 could offer great potential for the applications, such as catalytic supports, gas storage, lubricants, biomolecule adsorption and drug delivery.

## 6. REFERENCES

1. Sakamoto, Y.; Kaneda, M.; Terasaki, O.; Zhao,

- D.; Kim, J. M.; Stucky, G.; Shin, H. J.; Ryoo, R. *Nature* **2000**, *408*, 449.
2. Vinu, A.; Murugesan, V.; Hartmann, M. *Chem. Mater.* **2003**, *15*, 1385.
  3. Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrikson, G.; Chmelka, B.; Stucky, G.D. *Science* **1998**, *279*; Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
  4. Kim, T.-W.; Ryoo, R.; Kruk, M.; Gierszal, K. P.; Jaroniec, M.; Kamiya, S.; Terasaki, O. *J. Phys. Chem. B* **2004**, *108*, 11480.
  5. Kim, T.-W.; Ryoo, R.; Gierszal, K. P.; Jaroniec, M.; Solovyov, L. A. *J. Mater. Chem.* **2005**, *15*, 1560.
  6. Kawaguchi, M.; Yagi, S.; Enomoto, H. *Carbon* **2004**, *42*, 345.
  7. Khabashesku, V. N.; Zimmerman, J. L.; Margrave, J. L. *Chem. Mater.* **2000**, *12*, 3264.
  8. Qiu, Y.; Gao, L. *Chem. Commun.* **2003**, 2378.
  9. Sánchez-López, J. C.; Donnet, C.; Lefèbvre, F.; Fernández-Ramos, C.; Fernández, A. *J. Appl. Phys.* **2001**, *90*, 675.
  10. Marton, D.; Boyd, K. J.; Al-Bayati, A. H.; Todorov, S. S.; Rabalais, J. W. *Phys. Rev. Lett.* **1994**, *73*, 118.
  11. Chen, Y. H.; Tay, B. K.; Lau, S. P.; Shi, X.; Qiao, X. L.; Chen, J. G.; Wu, Y. P.; Sun, Z. H.; Xie, C. S. *J. Mater. Res.* **2002**, *17*, 521.
  12. Hellgren, N.; Guo, J.; Luo, Y.; Sâthe, C.; Agui, A.; Kashtanov, S.; Nordgren, J.; Ågren, H.; Sundgren, J. E. *Thin Solid Films* **2005**, *471*, 19.
  13. Kroke, E.; Schwarz, M. *Coordin. Chem. Rev.* **2004**, *248*, 493.
  14. Guo, Q.; Yang, Q.; Zhu, L.; Yi, C.; Zhang, S.; Xie, Y. *Solid State Commun.* **2004**, *132*, 369.
  15. Bai, Y.-J.; Lu, B.; Liu, Z.-G.; Li, L.; Cui, D.-L.; Xu, X.-G.; Wang, Q.-L. *J. Crystal Growth* **2003**, *247*, 505.
  16. Zimmerman, J. L.; Williams, R.; Khabashesku, V. N.; Margrave, J. L. *Nano. Lett.* **2001**, *12*, 731.
  17. Gillan, E. G. *Chem. Mater.* **2000**, *12*, 3906.
  18. Kouvetakis, J.; Bandari, A.; Todd, M.; Wilkens, B.; Cave, N. *Chem. Mater.* **1994**, *6*, 811.
  19. Wang, J.; Miller, D. R.; Gillan, E. G. *Carbon* **2003**, *41*, 2031.
  20. Vinu, A.; Ariga, K.; Mori, T.; Nakanishi, T.; Hishita, S.; Golberg, D.; Bando, Y. *Adv. Mater.* **2005**, *17*, 1648.
  21. Kim, J. M.; Sakamoto, Y.; Hwang, Y. K.; Kwon, Y.-U.; Terasaki, O.; Park, S.-E.; Stucky, G. D. *J. Phys. Chem. B.* **2002**, *106*, 2552.
  22. Ravikovitch, P.I.; Neimark, A.V. *Langmuir* **2002**, *18*, 1550.

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